

On the theory of dielectric relaxation

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Dielectric relaxation has been investigated within the framework of a modified mean field theory, in which two dynamic processes are believed to be involved in dielectric relaxation; the first corresponds to relaxation of crystalline lattice and the second represents slow relaxation of a partially ordered phase of high-temperature structure precursors generated by thermal fluctuations in solid dielectrics. It later becomes clear that it is the interaction between these two processes that results in a universal dielectric relaxation law.

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In 1913, Debye investigated the anomalous dispersion phenomenon, in which the corresponding index of refraction falls with frequency, of a group of dipolar molecules [1]; he treated a dipolar molecule of the group as a sphere immersed in a viscous fluid and then, under the assumption that the only electric field acting on the molecule is the external field, used Einstein's theory of Brownian motion [2, 3] to tackle the collisions between the molecule and its neighboring molecules in the liquid; eventually he formulated the following equation [1],

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau_c}, \quad (1)$$

where ε is the complex permittivity of the dipolar molecules and ω is the angular frequency of the external field; ε_∞ and ε_s represent the permittivity at the high frequency limit and the static permittivity of the dipolar molecules, respectively; τ_c is the characteristic relaxation time of the dipolar molecules. The above equation is often called the Debye relaxation law, which represents the dielectric relaxation response of the above-mentioned dipolar molecules to an alternating external electric field.

The dielectric relaxation phenomena had been extensively investigated long before the Debye law was proposed. Perhaps it is the first relaxation law that was derived soundly based on statistical mechanics, thus the Debye law is often regarded as the starting point for studying relaxation responses of dielectrics. Unfortunately, numerous experimental studies have shown clearly that the relaxation behavior of a wide range of dielectric materials deviates strongly from the Debye law. Over the past 70 years, many empirical relaxation laws, as the variants of the Debye law, have been developed. Among the most important are the Cole-Cole equation (1941-1942) [4, 5], the Cole-Davidson equation (1950-1951) [6, 7], the Havriliak-Negami equation (1966-1967) [8, 9], the Kohlrausch-Williams-Watts function (the Fourier transform of the stretched exponential function or the Kohlrausch function [10]) (1970) [11], etc. In practice, these empirical relationships work very well for certain materials, but not for others. In 1970s, Jonscher and his co-workers analyzed dielectric response data of around 400 hundred dielectric materi-

als and then he suggested that there exists a universal law of the dielectric response [12-16]. Largely due to Jonscher's pioneering work, people have noticed an interesting fact that the relaxation behavior is very similar despite different materials used and experimental techniques employed and most relaxation data can be interpreted by two types of experimental fitting function [17]: the Kohlrausch function or the stretched exponential function (1854) [10] (historically, the citations related to the Kohlrausch function might be confused; the corresponding clarification has been given in Ref. [18]), which is written below

$$f(x) \cong \exp \left[- \left(\frac{x}{\tau} \right)^\alpha \right] \quad 0 < \alpha < 1,$$

or the Jonscher function [14]

$$f(x) = \begin{cases} ax^m & 0 < m < 1, \\ bx^{n-1} & 0 < n < 1, \end{cases}$$

where τ , a , and b are parameters for a given material.

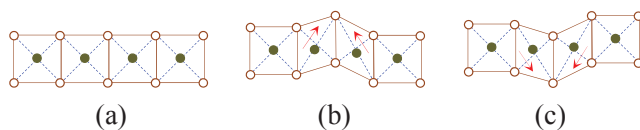


FIG. 1. Diagrammatic representation of normal and distorted crystal lattice; (a) normal crystal lattice without net dipole moment; (b) and (c) distorted crystal lattice with net dipole moment represented by arrows.

Surprisingly, the above-mentioned empirical laws or functions are all fractional power-law relationships. If a universal dielectric relaxation law does exist, then, at least, those laws or functions could be derived from the same fundamental equation. In this paper, we will attempt to find this fundamental equation and explore the physical mechanism underlying dielectric relaxation phenomena.

As usual, we start with the Debye law. It is generally believed that neglecting the mutual interactions between dipolar molecules and their neighboring molecules is the

reason that makes the Debye law deviate from experimental observations. The Debye law, however, is the model based on statistical mechanics, which is closely related to the Einstein theory of the brownian motion and the Smoluchowski equation [19]; like the collisions between dipolar molecules and their neighboring molecules, the interactions have been implicitly considered in Debye's model and the corresponding induced dipole moments have been assumed to be stochastic in the time domain and randomly distributed in the spatial domain so that the net influence of the interactions is zero. Therefore, the problem associated with the Debye law is not whether the interactions are neglected or not but what kinds of dipole moments can be induced by the interactions and cannot be averaged out. In other words, we have to take a close look at what kinds of dipole moments induced by the mutual interactions are neither purely stochastic in the time domain nor randomly distributed in the spatial domain and consider how they would behave and then alter dielectric relaxation processes during the perturbation of external electric fields. Obviously, if we try to solve the problem, we must consider the involved many-body problem. In his recent voluminous work, Ngai has repeatedly emphasized that the universal dielectric relaxation law, if it exists, must be built on the basis of the many-body problem [20]. Inspired by Ngai's profound insights on relaxation in complex systems, we will attempt to use a modified mean field theory (MMFT) to study the dielectric relaxation behavior.

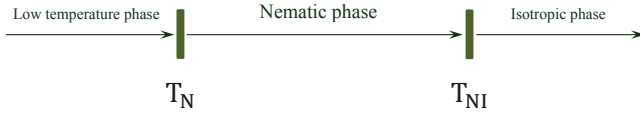


FIG. 2. Schematic representation of the cooperative behavior spectrum of HTSPs. Below temperature T_N and above temperature T_{NI} , there is no cooperative movement in HTSPs; between T_N and T_{NI} , HTSPs can behave cooperatively to form a nematic phase.

We now need to address how certain dipole moments could be induced and then explain what kinds of microscopic structures those dipole moments could form under an external electric field. For a crystalline material, it has a purely ordered structure at absolute zero and a completely disordered structure near its melting point; at temperatures between those two extremes, the material would possess both ordered and disordered structures largely due to thermal fluctuations (we here do not consider the defects and microscopic disordered structures generated during manufacturing processes in dielectric materials). Let's consider a crystalline dielectric lattice diagrammatically shown in Fig. [1]. Even at temperatures far below the melting point, there always exists the probability that certain atoms in the normal crystal lattice shown in Fig. [1a] could gain extra kinetic energy to move quasi-permanently away from their original equilibrium positions and distort crystal lattice as shown

in Figs. [1b] and [1c] due to thermal fluctuations. This kind of distortion can introduce the local non-uniform deformation, which breaks the inversion symmetry and induce dipole moments even in non-polar dielectric materials [21]; the induced dipole moments are schematically shown in Figs. [1b] and [1c]. The local disordered polar structures corresponding to such distorted crystal lattice are defined as high-temperature structure precursors (HTSPs). Since HTSPs possess higher potential energy, they are often metastable. Recent studies have shown that those polar HTSPs can form a partially ordered nematic phase over a wide temperature range from T_N to T_{NI} due to the competition between energy and entropy in dielectric materials [22]. If we use v to represent the local preferred direction and approximately treat HTSPs as molecules, then their orientational order parameter, S_{op} , can be written as [23, 24]

$$S_{op} = \frac{1}{2} \langle 3 (v^i, \vec{n})^2 - 1 \rangle = \frac{1}{2} \langle (3 \cos^2 \theta^i - 1) \rangle, \quad (2)$$

where $\langle \rangle$ represents the average; v^i is defined as the given direction of the disordered structure located at the position i ; \vec{n} is usually called the director that represents a particular direction; θ^i is defined as the angle between v^i and \vec{n} at the position i . If $0 < S_{op} < 1$, we can say that HTSPs cooperatively form a nematic phase. $S_{op} = 1$ corresponds to an ideal case, in which all HTSPs are perfectly aligned. If temperature continues to rise, at a certain point $T = T_{NI}$, the thermal energy will be large enough to disturb HTSPs, which makes HTSPs randomly oriented and then renders $S_{op} = 0$. Therefore, when $T > T_{NI}$, all HTSPs behave like a normal liquid, which has an isotropic phase. The cooperative behavior spectrum of HTSPs is shown schematically in Fig. [2].

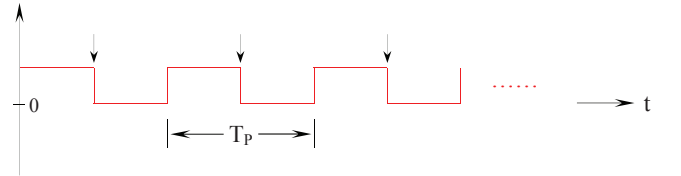


FIG. 3. Diagrammatic sketch of the loading signal; the characteristic relaxation occurs only once within one T_p , which is the period of the loading signal.

Within the framework of MMFT, the Gibbs free energy of a unit volume crystalline dielectric specimen containing polar HTSPs can be written as

$$G = U - TS - (1+k)ED = U - TS - (1+k) \frac{\varepsilon_r}{\varepsilon_0 \chi^2} P^2, \quad (3)$$

or

$$G = U - TS - (1-k)ED = U - TS - (1-k) \frac{\varepsilon_r}{\varepsilon_0 \chi^2} P^2, \quad (4)$$

where P and D represent the electric polarization and the electric displacement, respectively; ε_0 and ε_r represent the electric permittivity of free space and the relative

permittivity, respectively; χ is defined as electric susceptibility; E is the applied electric field; k here is defined as

$$k = \frac{k_0 S_{op}(T - T_N)}{T_N} \quad (T_N < T < T_{NI}), \quad (5)$$

where both k and k_0 are dimensionless coefficients. The physical meaning of k can be explained as following - it actually represents, in the statistical sense, the fraction of the potential energy, which is generated by the cooperative movement of polar HTSPs. The term $(1 + k)$ in Eq. (3) demonstrates that the crystalline and the nematic phases of the test specimen respond to an applied electric field, which often corresponds to the case that the field is too weak to disturb the nematic phase. However, the term $(1 - k)$ in Eq. (4) represents the situation that is often encountered in practice; the negative sign here is due to Le Chatelier's principle, which means that, if the applied field is large enough to be able to disturb the nematic phase, the nematic phase as the ensemble of polar HTSPs would then undergo a specific structural change, in which those polar HTSPs would tend to huddle together and grow up (this means that k will gradually increase when the external field is continually applied), to counteract any imposed polarization by the field [25]. Clearly, in either cases, the evolution of k during the perturbation of the applied field could alter the linear polarization-electric field relationship or the dielectric relaxation behavior of the test specimen. In order to determine how the relaxation behavior is influenced by k , we need to exploit a modified Landau-Khalatnikov equation, which is given below [26]

$$\gamma \frac{dP}{dt} = \frac{\partial G}{\partial P}, \quad (6)$$

where γ is a kinetic coefficient and is considered to be independent of temperature [24, 27]; t represents the time variable. We will consider the following two cases separately.

Case I - the applied electric field is weak and the term $(1 + k)$ is given in the Gibbs free energy. Substitute G given in Eq. (3) into Eq. (6), we get the following result

$$\gamma \frac{dP}{dt} = \frac{\partial G}{\partial P} = -2(1 + k) \frac{\varepsilon_r}{\varepsilon_0 \chi^2} P. \quad (7)$$

Solve this equation, we have,

$$P = P_s \exp \left[-\frac{2(1 + k)\varepsilon_r}{\gamma \varepsilon_0 \chi_e^2} t \right] = P_s \exp \left[-\frac{t}{\tau} \right], \quad (8)$$

where P_s is defined as the induced electric polarization under static electric fields and $\tau = \frac{\gamma \varepsilon_0 \chi_e^2}{2(1 + k)\varepsilon_r}$. If we further assume that $\tau_c = \frac{\gamma \varepsilon_0 \chi_e^2}{2\varepsilon_r}$ represents the characteristic relaxation time of the test specimen, then the relationship between τ and τ_c can be written as $\tau = \frac{\tau_c}{1 + k}$ or $\tau = (1 - k')\tau_c$, here $k' = k/(1 + k)$. Thus, t can be

defined as the modified characteristic relaxation time of the test specimen. Clearly, the above equation can be written in the following two forms.

$$\chi = \chi_s \exp \left[-\frac{t}{\tau} \right], \quad (9)$$

or

$$\varepsilon = \varepsilon_s \exp \left[-\frac{t}{\tau} \right], \quad (10)$$

where both χ_s and ε_s represent the static susceptibility and the static permittivity, respectively.

The above equations, Eqs. (8), (9), and (10), only represent a single modified characteristic relaxation after an instantaneous external perturbation. In order to investigate the dielectric relaxation behavior of the test specimen, we need to determine the relationship between the characteristic relaxation and the applied field. For this purpose, we consider the applied electric field that has the waveform that is shown schematically in Fig. [3]. If defining T_p as the period of the field, we can clearly see that it is a one-direction signal, in which there is no reversal and, if $T_p \gg \tau$, the characteristic relaxation will fully occur once at $\frac{T_p}{2}$ within one period. The dielectric relaxation of the test specimen under an applied electric field reduce to a continuous and progressive relaxation process consisting of a series of the modified characteristic relaxations. Obviously, there is a high frequency limit imposed by the test specimen itself. If the frequency of the applied field reaches this limit or approaches τ_c , the specimen cannot fully respond to the field and its relaxation will start to saturate. Without loss of generality, we define the value of ε at this limit as ε_∞ . Then Eq. (10) can be modified as

$$\frac{\varepsilon - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \exp \left[-\frac{t}{\tau} \right]. \quad (11)$$

We then take the Fourier transform of the right hand side of Eq. (11). The result is given below,

$$F \left[\exp \left(-\frac{t}{\tau} \right) u(t) \right] = \frac{\tau}{1 + i\omega\tau} \quad (\omega = 2\pi f), \quad (12)$$

here f is the frequency of the applied electric field. However, t in Eq. (11) actually varies from 0 to τ not from 0 to ∞ . We can imagine that we squeeze the waveform of the applied signal from $(0, \infty)$ to $(0, \tau)$ in the time domain and, let's say, if $\tau = 0$, then the squeezed waveform should behave like the Dirac delta function. We now modify Eq. (12) as follows

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{\tau} F \left[\exp \left(-\frac{t}{\tau} \right) u(t) \right] = \frac{1}{1 + i\omega\tau}, \quad (13)$$

where we can see that, when $\tau \rightarrow 0$, $(\varepsilon(\omega) - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty) = 1$, which is exactly the Fourier transform result

of the Dirac delta function. The above equation can be further expressed as

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + i\omega(1 - k')\tau_c}. \quad (14)$$

If $k = 0$, then $k' = 0$ so that this equation will reduce to Eq. (1), which is the mathematical expression of the Debye relaxation law [1].

If we assume that $k' \ll 1$, then $i\omega(1 - k')\tau_c$ can be simplified as $i\omega(1 - k')\tau_c \approx 1 - 1 + k' + (1 - k')i\omega\tau_c = 1 + (1 - k')[i\omega\tau_c - 1]$; here $\omega\tau_c < 1$ and, therefore, $|i\omega\tau_c - 1| < 1$. By taking advantage of Eq. (B1) in Appendix, we have $i\omega(1 - k')\tau_c \approx (i\omega\tau_c)^{1-k'}$, then Eq. (14) can be simplified as,

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau_c)^{1-k'}}, \quad (15)$$

which is the mathematical expression of the Cole-Cole equation [4, 5].

If k' is large enough and cannot be neglected, we can directly take advantage of Eq. (B1) in Appendix since $|i\omega\tau_c| < 1$. Then Eq. (14) can be re-written as

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{(1 + i\omega\tau_c)^{1-k'}}, \quad (16)$$

which is the mathematical expression of the Cole-Davidson equation [6, 7].

In Eq. (16), if we further assume that there exists k'' and $k'' \ll 1$, then $1 - k'' \approx 1$. We then have $i\omega\tau_c \approx i(1 - k'')\omega\tau_c$. By using the same approach exploited in deriving the Cole-Cole equation, we can get $i\omega\tau_c \approx i(1 - k'')\omega\tau_c \approx (i\omega\tau_c)^{1-k''}$. Substitute this expression into Eq. (16), we have the following relationship:

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{[1 + (i\omega\tau_c)^{1-k''}]^{1-k'}}, \quad (17)$$

which is the mathematic expression of the Havriliak-Negami equation [8, 9].

Case II - the applied electric field is large enough to be able to disturb the nematic phase and the term $(1 - k)$ is given in the Gibbs free energy. By using the same deriving method, we can get the following result.

$$\frac{\varepsilon - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \exp \left[-(1 - k) \left(\frac{t}{\tau_c} \right) \right]. \quad (18)$$

Since $t \in (0, \tau_c)$ and $\frac{t}{\tau_c} < 1$, we can write $(1 - k) \left(\frac{t}{\tau_c} \right) + k = 1 + (1 - k) \left(\frac{t}{\tau_c} - 1 \right)$. Obviously, $|\frac{t}{\tau_c} - 1| < 1$. By taking advantage of Eq. (B1) in Appendix, we can get $(1 - k) \left(\frac{t}{\tau_c} \right) + k \approx \left(\frac{t}{\tau_c} \right)^{1-k}$. Then the above equation can be re-written as

$$\frac{\varepsilon - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = C \exp \left[- \left(\frac{t}{\tau_c} \right)^{1-k} \right], \quad (19)$$

where $C = \exp[k]$. This equation is the mathematic expression of the Kohlrausch function or the stretched exponential function [10]. Therefore, the Kohlrausch-Williams-Watts function (the Fourier transform of the Kohlrausch function), which was first used by Williams and Watts [11], can be simplified as

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{C}{1 + i\omega\tau} = \frac{C(1 - k)}{(1 - k) + i\omega\tau_c}, \quad (20)$$

where $\tau = \frac{\tau_c}{1-k}$.

Concluding remarks - it is perhaps safe to say now that the key factor making the Debye law deviate strongly from the relaxation behavior of most dielectric materials is that the cooperative movement of polar HTSPs has been neglected in previous studies. In view of what have been derived and discussed above, we believe that there are two dynamic processes involved in dielectric relaxation. the first corresponds to relaxation of crystalline lattice and the second represents slow relaxation of a partially ordered phase of polar HTSPs in solid dielectrics. The universal dielectric relaxation law does exist. All dielectric relaxation relationships including the Debye law are just the variants of this universal law under different situations.

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Appendix A: Binomial series expansion

For a function $f(x) = (1 + x)^\xi$, its binomial series expansion can be written as

$$(1 + x)^\xi = 1 + \xi x + \frac{\xi(\xi - 1)}{2!}x^2 + \frac{\xi(\xi - 1)(\xi - 2)}{3!}x^3 + \dots + \frac{\xi(\xi - 1) \cdots (\xi - n + 1)}{n!}x^n + \dots,$$

here, for simplicity, we only consider the case, in which ξ is a real number. If $|x| < 1$, the above series will converge absolutely for any number ξ and, thus, can be simplified to the following linear equation.

$$(1 + x)^\xi \approx 1 + \xi x. \quad (B1)$$

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